Coulomb potentials in two and three dimensions under periodic boundary conditions

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Abstract

A method to sum over logarithmic potential in 2D and Coulomb potential in 3D with periodic boundary conditions in all directions is given. We consider the most general form of unit cells, the rhombic cell in 2D and the triclinic cell in 3D. For the 3D case, this paper presents a generalization of Sperb's work [R. Sperb, Mol. Simulation, **22**, 199-212(1999)]. The expressions derived in this work converge extremely fast in all region of the simulation cell. We also obtain results for slab geometry. Furthermore, self-energies for both 2D as well as 3D cases are derived. Our general formulas can be employed to obtain Madelung constants for periodic structures.

I. INTRODUCTION

It has become a common practice to employ numerical simulations in the study of physical problems, which are difficult to solve analytically. Since it is not possible to simulate realistic physical systems, containing ions of the order of Avogadro number, one usually works with a very small system. For small systems, containing a few hundred to a few thousand charges, boundary effects become relatively pronounced, especially if the nature of interaction is long range. To avoid this problem, periodic boundary conditions (PBC) are usually employed. In many simulations, the nature of interaction is such that the potential satisfies the Poisson equation. For example, a logarithmic interaction in two dimensions (2D) and a Coulomb potential in three dimensions (3D) both satisfy the Poisson equation in 2D and 3D respectively. We refer to a potential which goes as $r^{(-d+2)}$ in a $d \geq 2$ dimensional isotropic space as a Coulomb type potential. The Coulomb type potentials fall under the category of long range potentials. In fact, in a $d \geq 2$ dimensional space, any interaction which goes as $r^{-\alpha}$, where $\alpha < (d-1)$ is known as a long range interaction. The reason being, while the potential decays as $r^{-\alpha}$, the volume element goes as $r^{(d-1)}$. As a result, in a periodic system, even charges located at infinity give rise to a finite contribution to energy and forces, which cannot be neglected. We consider Coulomb type of potentials in 2D and 3D in this paper.

To derive a formula for interaction between two particles with PBC imposed, one has to consider the interaction of a particle with periodic repetitions of itself, as well as that of the second particle. Interaction energy of a particle with its own periodic repetitions is termed as the self-energy. Determination of self-energy is important in simulations where the size of simulation box may change during the simulation. For example, such a case arises in an isobaric Monte Carlo simulation. The aim of this paper is to consider the kind of interactions mentioned above for the most general type of unit cells in 2D and 3D. We consider a rhombic unit cell in 2D and a triclinic cell in 3D, with origin lying at the bottom left corner of the unit cell. The unit cell contains a number of ions, which interact via Coulomb type potential, satisfying the Poisson equation in their respective dimensions. The unit cell repeats itself in all directions under PBC. Hence, the interaction of a particle located at $\mathbf{r}$ with another particle located at the origin includes, apart from the direct interaction between the two particles, the interaction of the first particle with all periodic images of the second particle.

These periodic images of the second particle are located at lattice vector sites given by $\mathbf{l} = m\mathbf{a} + n\mathbf{b} + p\mathbf{c}$, where m, n and p range from $-\infty$ to $+\infty$. Also, the particle interacts with its own images located at $\mathbf{r}+\mathbf{l}$, where $\mathbf{l}$ is defined as above. Thus, if we have N charges q_i in a charge neutral unit cell, then the Coulomb energy may be written as

$$E = \frac{1}{2} \sum_{\mathbf{n}\in\mathbb{Z}^3}{}' \sum_{i,j=1}^{N} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}|}, \tag{1.1}$$

where a prime indicates that $\mathbf{n} = 0$ term is to be excluded for the case when $i = j$. The series in Eq.(1.1) is a conditional series. This series can be summed up to any value depending on the order in which the terms of the series are grouped. Therefore, a summation convention has to be specified based on the physical nature of the problem in mind.

The conditional series mentioned above may be evaluated by introducing background charges in a way that the total background charge adds up to zero. Imposing background charges in this way leads to well defined ways of summing the conditional series. However, results of the summation of conditional series may still differ in view of the method employed to impose background charges, as the background charges may have a structure of their own. For example, background charges in a 3D system with PBC may be imposed in the following two ways. A charge q and all its periodic repetitions under the PBC may be viewed as a set of layers along an axis of the unit cell. In order to impose background charge on this system, we may assume that all these different layers are charge neutral separately. Thus, we may assume that for a layer composed of charge q and its periodic images, one has an additional uniform charge density of $-q/a$, where a is the area of the 2D unit cell. Thus the overall charge contained in each 2D cell of the layer is zero. Another charge q' present in the system will interact with the set of charges q as well as the neutralizing background surface charge with charge density. However, it can be shown that introducing these uniform background charge sheets leads to some unwanted terms, as the sheets have a structure of their own.

However, there is a better way of imposing background charges, without introducing any structure of the background charges themselves. This can be achieved by distributing a uniform 3D charge on the grid made out of charge q and its images. The neutralizing background charge now has a uniform charge density of $-q/V$, where V is the volume of the unit cell. This volume charge adds up to zero at any point due to the overall charge neutrality condition and thus does not introduce any artificial structure, such as the uniform sheets in the previous case.

The results of the two prescriptions suggested above differ by two terms. The first term depends on the square of the component of the dipole moment[15], along the direction of layering, of the original charges contained in the unit cell. The second term depends linearly on the distance between the pair of charges along the direction of layering.

In this paper, we adopt the second procedure. Using the results derived here, it will be easy to establish connection between the results of two summation conventions mentioned above. Introduction of neutralizing charge background in the form of a uniform cloud leads to only the intrinsic part[1] of potential energy and this technique has previously been employed by Lekner[1] and Sperb[2]. It is important to know that the two procedures mentioned above still do not lead to the correct energy of a collection of charges interacting under the PBC, if one wants a limit of spherical means[2]. De Leeuw *et. al*[3] have shown that for 3D case, an extra term depending on the total dipole moment of the unit cell has to be added to get the correct energy of charges. For the 2D case the correction term turns out to be zero.

With the help of discussion above, the energy of N particles contained in a unit cell with periodic boundaries and interacting through a Coulomb type potential in 3D can be expressed as,

$$E_{\text{total}} = \frac{1}{2}\sum_{i,j;i\neq j} q_i q_j G(\mathbf{r}_i - \mathbf{r}_j) + \sum_i q_i^2 G_{\text{self}} + \frac{2\pi}{3}\left(\sum_i q_i \mathbf{r}_i\right)^2 . \tag{1.2}$$

Here the charges are denoted by q_i's and their positions in the unit cell by $\mathbf{r}_i$'s and $1 \leq i \leq N$. The last term in Eq.(1.2) is the dipole term introduced by De Leeuw *et. al*[3] . For the 2D case one has only the first two terms on the right hand side. Our aim in this paper is to obtain expressions for $G(\mathbf{r})$ and G_{self} in 2D and 3D.

Before proceeding further, we briefly discuss three main approaches in use to obtain Coulomb interaction with periodic boundaries. These three approaches are due to Ewald[4], Lekner[1,5] and Sperb[2]. The Ewald method was developed eighty years ago in connection with the evaluation of Madelung constants. This method, in spite of its shortcomings, is still very much in use. The method proceeds by breaking the original summation in two parts. One of these sums is carried out in real space and another one in Fourier space. This splitting of summation depends on a real parameter which has to be chosen judiciously, failing which the series in real and Fourier space might converge very slowly. In general, to calculate a pair-wise interaction it usually requires a few hundred terms involving complementary error functions.

An alternative to the Ewald method was given by Lekner[1]. This method involves an evaluation of a few dozen terms if the position vector $\mathbf{r}$ is not very small. If $\mathbf{r}$ tends to zero this method converges slowly. The problem of convergence was fixed later by Lekner in another paper[5], following Sperb's work[6]. Lekner method has not been generalized to a triclinic cell yet. Though, it is possible to generalize Lekner's work for a triclinic cell, here, we take a different approach along the lines of Ref.7 to obtain results for a triclinic cell.

Among the latest advances on Coulomb sums is by Grønbech-Jensen[8] in 2D and Sperb[2] in 3D. Sperb's results are similar to that of Harris *et al.*[9] and Crandall *et al.*[10]. A major advantage of Sperb's work is that it can be employed to get $N \ln(N)$ scaling in time[11], where N is the number of ions present in the system. On the other hand, with Ewald summation method, one can get only $[N \ln(N)]^{3/2}$ scaling[12]. In this paper, our aim is to generalize Sperb's work[2] to a triclinic cell. The method given in this work will contain Sperb's result in a simplified form as a special case. Also for the first time, an alternative to Ewald's technique will be given, which can be applied to the most general kind of unit cell in a computer simulation, a triclinic unit cell. We will also discuss scaling of $N \ln(N)$ that may be achieved with the use of formulas developed here.

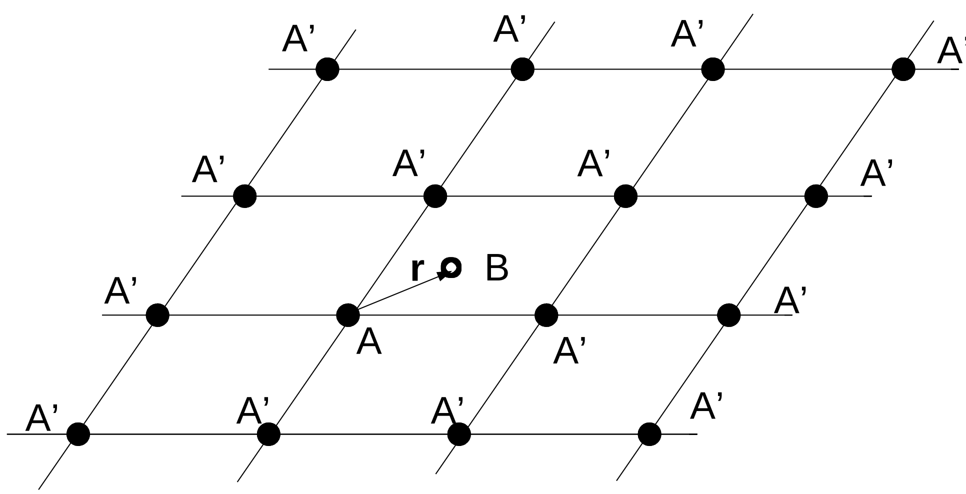

FIG. 1: A schematic diagram explaining the set of for a 2D rhombic cell. A charge located at B interacts with another charge located at the origin A as well as its periodic images located at A's.

II. LOGARITHMIC INTERACTION IN 2D

An excellent method to sum over Coulomb type potential (logarithmic interaction) in 2D was given by Grønbech-Jensen[8]. Another alternative was provided by Tyagi *et al.*[13] in a recent paper. The problem with the later approach is that the lattice sum does not converge when the two charges are close together within the unit cell. This problem will be addressed here and formulas will be modified in such a way that the convergence is achieved for even those cases where charges are close to each other. Thus we will obtain a result which is different from Grønbech-Jensen but still as efficient.

We consider a rhombic cell with periodic boundaries along the x and y directions. A sketch of the cell is shown in Fig. 1. A particle, located at position $\mathbf{r}$, interacts logarithmically with charges located at the vertices of a rhombic grid. A formula was developed in Ref.13 to compute this sum. We sketch a portion of that derivation here for the sake of completeness. Consider the Poisson equation in 2D:

$$\nabla^2 G(\mathbf{r}) = -2\pi \sum_{l} \delta(\mathbf{r} + \mathbf{l}) + \frac{2\pi}{l_1 l_2 \sin\theta}. \tag{2.1}$$

The second term on the right hand side amounts to the presence of a neutralizing background charge. The solution of Eq. (2.1) is given by

$$G(\mathbf{r}) = \frac{2\pi}{l_1 l_2 \sin\theta} \lim_{\xi\to 0} \left(\sum_{\mathbf{Q}} \frac{\exp(i\mathbf{Q}\cdot\mathbf{r})}{\mathbf{Q}^2 + \xi^2} - \frac{1}{\xi^2} \right), \tag{2.2}$$

where l_1 and l_2 denote the lengths of the sides of the rhombic cell and

$$\mathbf{r} = r_1\mathbf{e}_1 + r_2\mathbf{e}_2, \quad \mathbf{Q} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2. \tag{2.3}$$

Here, $0 \le r_1 < l_1$, $0 \le r_2 < l_2$ and $\mathbf{e}_1$ and $\mathbf{e}_2$ represent the unit vectors along the axis of the rhombic cell, with $\mathbf{e}_1.\mathbf{e}_2 = \cos\theta$. We have also introduced an infinitesimal parameter ξ. The sum over $\mathbf{Q}$ runs over all reciprocal lattice vectors spanned by

$$\mathbf{b}_i = \frac{2\pi}{l_i \sin^2\theta}(\mathbf{e}_i - \mathbf{e}_j \cos\theta), \tag{2.4}$$

for $(i,j) = (1,2),(2,1)$ and n_1 and n_2 are integers. Introduction of an infinitesimal parameter ξ as in Eq. (2.2) implies assumption of the presence of a neutralizing background charge. Thus, here a charge q located at (x,y) in the unit rhombic cell interacts with charges q'

located at the origin and all other vertices of the grid. The charge q also interacts with a uniform layer of background charge superimposed on the grid of q' charges such that the charge density is $-q'/a$, where $a = l_1 l_2 \sin\theta$, is the area of the unit cell. From now onward we will always assume that a final limit $\xi \to 0$ is to be taken. Using the value $\mathbf{Q}$ from Eq.(2.3) and Eq.(2.4) in Eq.(2.2) we obtain

$$G(\mathbf{r}) = \frac{\sin\theta}{2\pi l_1 l_2} \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \frac{\exp\left[i2\pi\left(n_1\frac{r_1}{l_1} + n_2\frac{r_2}{l_2}\right)\right]}{\left(\frac{n_1}{l_1}\right)^2 - 2\frac{n_1}{l_1}\frac{n_2}{l_2}\cos\theta + \left(\frac{n_2}{l_2}\right)^2 + \frac{\xi^2}{l_1 l_1}} - \frac{\sin\theta}{2\pi\sigma}\frac{1}{\xi^2},$$

where $0 \leq r_i/l_i < 1$, $\sigma = l_2/l_1$ and we have redefined infinitesimal parameter ξ for sake of calculations. We now evaluate the sum

$$\begin{aligned} f(n_1, \xi) &= \sum_{n_2=-\infty}^{\infty} \frac{\exp\left(i\frac{2\pi}{l_2} n_2 r_2\right)}{\left(\frac{n_1}{l_1}\right)^2 - 2\frac{n_1}{l_1}\frac{n_2}{l_2}\cos\theta + \left(\frac{n_2}{l_2}\right)^2 + \frac{\sigma^2\xi^2}{l_2^2}} \qquad (2.5) \\ &= l_2^2 \sum_{n_2=-\infty}^{\infty} \frac{\exp\left(i\frac{2\pi}{l_2} n_2 r_2\right)}{n_1^2\sigma^2 - 2n_1 n_2 \sigma\cos\theta + n_2^2 + \sigma^2\xi^2} \\ &= \pi l_2^2 \exp(i2\pi\beta_{n_1} t_2) \frac{\exp(-i2\pi\beta_{n_1})\sinh[\gamma_{n_1} t_2] + \sinh[2\pi\gamma_{n_1}(1-t_2)]}{\gamma_{n_1}[\cosh(2\pi\gamma_{n_1}) - \cos(2\pi\beta_{n_1})]}, \end{aligned}$$

where $t_2 = r_2/l_2$,

$$\beta_n = n\sigma\cos\theta, \;\; \gamma_n = \sigma\sqrt{(n^2\sin^2\theta + \xi^2)}, \qquad (2.6)$$

and we have used the identity (here $\alpha < 2\pi$)

$$\sum_{n=-\infty}^{\infty} \frac{\exp(in\alpha)}{(n-\beta)^2 + \gamma^2} = \frac{\pi}{\gamma} \frac{\exp[i\beta(\alpha - 2\pi)]\sinh(\gamma\alpha) + \exp(i\beta\alpha)\sinh[\gamma(2\pi - \alpha)]}{\cosh(2\pi\gamma) - \cos(2\pi\beta)}, \qquad (2.7)$$

which is derived in Appendix A. The sum defined in Eq.(2.5) can be written as

$$\begin{aligned} G(\mathbf{r}) = &\frac{\sigma\sin\theta}{2} \sum_{n=-\infty}^{+\infty} \exp[i2\pi(nt_1 + \beta_n t_2)] \qquad (2.8) \\ &\times \frac{\exp(-2\pi\beta_n)\sinh(2\pi\gamma_n t_2) + \sinh[2\pi\gamma_n(1-t_2)]}{\gamma_n[\cosh(2\pi\gamma_n) - \cos(2\pi\beta_n)]} - \frac{\sin\theta}{2\pi\sigma}\frac{1}{\xi^2}, \end{aligned}$$

where $t_1 = r_1/l_1$. Separating out the term corresponding to $n = 0$, we obtain

$$G(\mathbf{r}) = \frac{\sigma \sin\theta}{2} \left(\frac{\sinh(2\pi\xi t_2) + \sinh[2\pi\xi(1-t_2)]}{\xi [\cosh(2\pi\xi) - 1]} \right) - \frac{\sin\theta}{2\pi\sigma} \frac{1}{\xi^2} \tag{2.9}$$
$$+ \frac{\sigma \sin\theta}{2} \sum_n{}' \exp(i2\pi n t) \frac{\exp(-2\pi\beta_n)\sinh(2\pi\gamma_n t_2) + \sinh[2\pi\gamma_n(1-t_2)]}{\gamma_n [\cosh(2\pi\gamma_n) - \cos(2\pi\beta_n)]},$$

where $t = t_1 + t_2\sigma\cos\theta$ and a prime on the summation sign indicates that the term corresponding to $n = 0$ is not to be included. Taking the limit $\xi \to 0$, one obtains

$$\lim_{\xi\to 0} \left(\frac{\sinh[2\pi\xi\sigma t_2] + \sinh[2\pi\xi\sigma(1-t_2)]}{\xi\sigma[\cosh(2\pi\xi\sigma) - 1]} - \frac{1}{\pi\sigma^2\xi^2} \right) = \frac{\pi}{3}\left(1 - 6t_2 + 6t_2^2\right). \tag{2.10}$$

Thus we obtain the following expression for $G(\mathbf{r})$

$$G(\mathbf{r}) = \frac{\sigma\sin\theta}{2}\frac{\pi}{3}\left(1 - 6t_2 + 6t_2^2\right) \tag{2.11}$$
$$+ \frac{\sigma\sin\theta}{2} \sum_n{}' \exp(i2\pi n t) \frac{\exp(-i2\pi\beta_n)\sinh(2\pi\gamma_{n0}t_2) + \sinh[2\pi\gamma_{n0}(1-t_2)]}{\gamma_{n0}[\cosh(2\pi\gamma_{n0}) - \cos(2\pi\beta_n)]},$$

where $\gamma_{n0} = \sigma|n\sin\theta|$. Due to the symmetrical nature of the unit cell, it suffices to look at only that part of the unit cell, which corresponds to $0 \le t_1 \le 0.5$ and $0 \le t_2 \le 0.5$. Eq. (2.11) fails to converge fast enough when $t_2 \to 0$. This problem can be easily fixed as follows. We add and subtract the following term from Eq. (2.11)

$$h(t, t_2) = \frac{1}{2}\sum_n{}' \frac{\exp(-2\pi\gamma_{n0}t_2)\exp(2\pi i n t)}{|n|}. \tag{2.12}$$

The quantity $h(t, t_2)$ can be easily evaluated by carrying out the sum in Eq. (2.12) analytically. Using the identity

$$\sum_{n=1}^{+\infty} \frac{\exp(-n|a|)\cos(nb)}{n} = -\frac{1}{2}\ln[\cosh(a) - \cos(b)] - \frac{\ln(2)}{2} + \frac{|a|}{2}, \tag{2.13}$$

one obtains

$$h(t, t_2) = -\frac{1}{2}\ln(\cosh[2\pi t_2\sigma\sin\theta] - \cos[2\pi t]) \tag{2.14}$$
$$- \frac{\ln(2)}{2} + \frac{2\pi\sigma t_2\sin\theta}{2}.$$

Thus we can write

$$
\begin{aligned}
G(\mathbf{r}) =& \frac{\sigma \sin \theta}{2} \frac{\pi}{3} \left(1 - 6t_2 + 6t_2^2\right) \\
& - \frac{1}{2} \ln \left(\cosh[\sigma \sin(\theta)\, 2\pi t_2] - \cos[2\pi t]\right) + \frac{2\pi\sigma t_2 \sin\theta}{2} - \frac{\ln(2)}{2} \\
& \times \frac{1}{2} \sum_n{}' \exp(i2\pi n t) \left\{ \frac{\exp(-i2\pi\beta_n)\sinh(2\pi\gamma_{n0}t_2) + \sinh\left[2\pi\gamma_{n0}(1-t_2)\right]}{|n| \left[\cosh(2\pi\gamma_{n0}) - \cos(2\pi\beta_n)\right]} \right. \\
& \left. - \frac{\exp(-2\pi\gamma_{n0}t_2)}{|n|} \right\},
\end{aligned}
\tag{2.15}
$$

After some effort, the above equation can be written as

$$
\begin{aligned}
G(\mathbf{r}) =& \frac{\sigma \sin\theta}{2}\frac{\pi}{3}\left(1 + 6t_2^2\right) - \frac{1}{2}\ln\left(\cosh\left[2\pi\sigma\sin(\theta)\, t_2\right] - \cos\left[2\pi t\right]\right) \\
& - \frac{\ln(2)}{2} + \sum_{n=1}^{+\infty} \left\{\cos\left[2\pi\left(nt - \beta_n\right)\right]\sinh(2\pi\gamma_{n0}t_2) + \cos(2\pi n t)\right. \\
& \times \left.\left[\exp\left(-2\pi\gamma_{n0}t_2\right)\cos\left(2\pi\beta_n\right) - \exp\left(-2\pi\gamma_{n0}\right)\cosh\left(2\pi\gamma_{n0}t_2\right)\right]\right\} / \\
& \left\{n\left[\cosh(2\pi\gamma_{n0}) - \cos(2\pi\beta_n)\right]\right\}.
\end{aligned}
\tag{2.16}
$$

Equation (2.16) converges extremely fast for all values of $0 \leq t_2 \leq 0.5$. However, to achieve better convergence the sides of the rhombic cell should be labelled such that $\sigma = l_2/l_1 \geq 1$. Now, an expression for the self-energy can be easily obtained by taking the limits $t_1 \to 0$ and $t_2 \to 0$ and subtracting

$$
g(\mathbf{r}) = -\frac{1}{2}\ln\left(r_1^2 + r_2^2 + 2r_1r_2\cos\theta\right), \tag{2.17}
$$

one obtains

$$
\begin{aligned}
G_{2\mathrm{d}}^{\mathrm{self}} =& \lim_{\mathbf{r}\to 0}\left(G(\mathbf{r}) - g(\mathbf{r})\right) \\
=& \frac{\sigma\sin\theta}{2}\frac{\pi}{3} + \sum_{n=1}^{+\infty}\left(\frac{\sinh(2\pi\gamma_{n0})}{n\left[\cosh(2\pi\gamma_{n0}) - \cos(2\pi\beta_n)\right]} - \frac{1}{n}\right) \\
& - \lim_{\mathbf{r}\to 0}\left(\frac{1}{2}\ln\left[(2\pi t_2\sigma\sin\theta)^2 + (2\pi t)^2\right] - \frac{1}{2}\ln\left[r_1^2 + r_2^2 + 2r_1r_2\cos\theta\right]\right) \\
=& \frac{\sigma\sin\theta}{2}\frac{\pi}{3} - \ln(2\pi l_1) - \sum_{n=1}^{+\infty}\left(\frac{\exp(-2\pi\gamma_{n0}) - \cos(2\pi\beta_n)}{n\left[\cosh(2\pi\gamma_{n0}) - \cos(2\pi\beta_n)\right]}\right).
\end{aligned}
\tag{2.18}
$$

III. COULOMB INTERACTION IN 3D

The Poisson equation to be solved in this case is

$$\nabla^2 G(\mathbf{r}) = -4\pi \sum_l \delta(\mathbf{r}+\mathbf{l}) + \frac{4\pi}{V}, \tag{3.1}$$

where

$$V = l_1 l_2 l_3 \left[\mathbf{e}_i.(\mathbf{e}_j \times \mathbf{e}_k)\right] \tag{3.2}$$

stands for the volume of the unit cell. The last term in Eq.(3.1) amounts to the presence of uniform background charge. The solution of Eq.(3.1) is given by

$$G(\mathbf{r}) = \frac{4\pi}{V} \lim_{\xi \to 0} \left(\sum_{\mathbf{Q}} \frac{\exp(i\mathbf{Q}\cdot\mathbf{r})}{\mathbf{Q}^2 + \xi^2} - \frac{1}{\xi^2} \right), \tag{3.3}$$

where

$$\mathbf{r} = r_1\mathbf{e}_1 + r_2\mathbf{e}_2 + r_3\mathbf{e}_3, , \quad \mathbf{Q} = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3, \tag{3.4}$$

where $\mathbf{Q}$ runs over all reciprocal lattice vectors spanned by

$$\mathbf{b}_i = \frac{2\pi}{l_i} \frac{\mathbf{e}_j \times \mathbf{e}_k}{\mathbf{e}_i.(\mathbf{e}_j \times \mathbf{e}_k)}, \tag{3.5}$$

for all cyclic permutations of (i,j,k) and n_1,n_2 and n_3 range from $-\infty$ to $+\infty$. Using Eqs.(3.3),(3.4) and (3.5) we obtain

$$\begin{aligned} G(\mathbf{r}) = {} & \frac{4\pi}{Vb_3^2} \sum_{n_1,n_2,n_3} \frac{\exp\left[i2\pi\left(n_1\frac{r_1}{l_1} + n_2\frac{r_2}{l_2} + n_3\frac{r_3}{l_3}\right)\right]}{(n_3^2 + n_2^2c_{22} + n_1^2c_{11} + 2n_1n_2c_{12} + 2n_2n_3c_{23} + 2n_3n_1c_{31} + \xi^2)} \\ & - \frac{4\pi}{Vb_3^2}\frac{1}{\xi^2}, \end{aligned} \tag{3.6}$$

where $0 \le r_i/l_i < 1$,

$$c_{ij} = \frac{\mathbf{b}_i.\mathbf{b}_j}{\mathbf{b}_3.\mathbf{b}_3} \qquad\qquad 1 \le i,j \le 3, \tag{3.7}$$

and we have, as before, introduced an infinitesimal parameter ξ in the denominator and subtracted a counter term from the whole sum due to the presence of a uniform background charge. We now evaluate the sum

$$L(n_1, n_2, r_3, \xi) = \frac{1}{\pi} \sum_{n_3=-\infty}^{\infty} \frac{\exp\left(i\frac{2\pi}{l_3}n_3r_3\right)}{(n_3^2 + n_2^2c_{23} + n_1^2c_{13} + 2n_1n_2c_{12} + 2n_2n_3c_{23} + 2n_3n_1c_{31} + \xi^2)}. \tag{3.8}$$

This sum can be obtained easily and the result is

$$\begin{aligned} & L(n_1, n_{2,} r_3, \xi) \qquad (3.9) \\ & = \exp(i2\pi\beta_{n_1,n_2} t_3) \frac{\exp\left[-i2\pi\beta_{n_1,n_2}\right] \sinh(2\pi\gamma_{n_1,n_2} t_3) + \sinh\left[2\pi\gamma_{n_1,n_2}(1-t_3)\right]}{\gamma_{n_1,n_2}\left[\cosh(2\pi\gamma_{n_1,n_2}) - \cos(2\pi\beta_{n_1,n_2})\right]} \end{aligned}$$

where

$$t_i = \frac{r_i}{l_i} \qquad \text{for } i = 1, 2 \text{ and } 3, \tag{3.10}$$

$$\beta_{n_1,n_2} = -n_1 c_{31} - n_2 c_{32}, \tag{3.11}$$

and

$$\gamma_{n_1,n_2} = \left[n_2^2 c_{22} + n_1^2 c_{11} + 2n_1 n_2 c_{12} - (n_1 c_{31} + n_2 c_{32})^2 + \xi^2\right]^{1/2}. \tag{3.12}$$

Plugging the value of $L(n_1, n_{2,} r_3, \xi)$ from Eq. (3.9) in Eq. (3.6) we obtain,

$$\begin{aligned} G(\mathbf{r}) &= \frac{4\pi^2}{V b_3^2} \sum_{n_1,n_2} \exp\left[i2\pi(n_1 t_1 + n_2 t_2)\right] \; L(n_1, n_{2,} r_3, \xi) - \frac{4\pi}{V b_3^2} \frac{1}{\xi^2} \qquad (3.13) \\ &= \frac{4\pi^2}{V b_3^2} \sum_{n_1,n_2}' \exp\left[i2\pi(n_1 t_1 + n_2 t_2)\right] \; L\left(n_1, n_{2,} r_3, \xi\right)\Big|_{\xi=0} \\ &+ \frac{4\pi^2}{V b_3^2} \frac{\pi}{3} \left(1 - 6t_3 + 6t_3^2\right) \ , \end{aligned}$$

where a prime over summation sign implies n_1 and n_2 cannot both be zero simultaneously. We have also separated out the term corresponding to $n_1 = 0$ and $n_2 = 0$ in Eq.(3.13) and taken the limit $\xi \to 0$, which results in cancellation of the diverging factor $4\pi/\left(V b_3^2 \xi^2\right)$. Eq. (3.13) is one of the main results of this paper. It is easy to see that the sum defined in Eq.(3.13) fails to converge fast enough as t_i tend to zero. In fact, towards large values of γ_{n_1,n_2}, the quantity L defined in Eq.(3.13) goes as $\exp\left(-2\pi\gamma_{n_1,n_2} t_3\right)$ and if t_3 is small, this convergence may be very slow. As before for the 2D case, we only concentrate on that part of unit cell which corresponds to $0 \leq t_i \leq 0.5$. To transform Eq. (3.13) in a form, which converges even for small values of t_i, we need to separate out a term which corresponds to slab geometry. By slab geometry we mean a situation which is obtained by sending one of

the sides of the unit cell to infinity. We write

$$G(\mathbf{r}) = \frac{4\pi^2}{Vb_3^2} \sum_{n_1,n_2}{}' \exp\left[i2\pi(n_1t_1+n_2t_2)\right] \; B\left(n_1,n_{2,}r_3,\xi\right)\Big|_{\xi=0} + G_2(\mathbf{r}) \tag{3.14}$$

$$+\frac{4\pi^2}{Vb_3^2}\frac{\pi}{3}\left(1+6t_3^2\right), \tag{3.15}$$

where G_2 corresponds to the slab geometry case and is given by,

$$\begin{aligned} G_2(\mathbf{r}) = {} & \frac{4\pi^2}{Vb_3^2} \sum_{n_1,n_2}{}' \frac{\exp\left[i2\pi\beta_{n_1,n_2}t_3 + i2\pi(n_1t_1+n_2t_2)\right]\exp(-2\pi\gamma_{n_1,n_2}t_3)}{\gamma_{n_1,n_2}} \\ & -\frac{4\pi^2}{Vb_3^2}\frac{\pi}{3}\left(6t_3\right), \end{aligned} \tag{3.16}$$

and B is defined as

$$B(n_1,n_{2,}r_3,\xi) = L(n_1,n_{2,}r_3,\xi) - \frac{\exp(i2\pi\beta_{n_1,n_2}t_3)\exp(-2\pi\gamma_{n_1,n_2}t_3)}{\gamma_{n_1,n_2}}. \tag{3.17}$$

The result in Eq.(3.16) represents Coulomb interaction with open boundary condition along the r_3 direction and periodic boundaries along the r_1 and r_2 directions. G_2 can be obtained from G by taking the limit $l_3 \to \infty$ and dropping a constant term. We also note above that both $(\beta_{n_1 n_2}t_3)$ and $(\gamma_{n_1,n_2}t_3)$ are independent of l_3, when $\xi \to 0$.

The term in Eq.(3.17), can be written as

$$\begin{aligned} & B(n_1,n_{2,}r_3,\xi) \\ & = -\frac{\exp\left(i2\pi\beta_{n_1,n_2}t_3\right)\left[\cosh\left[2\pi\left(i\beta_{n_1,n_2}-\gamma_{n_1,n_2}t_3\right)\right] - \exp(-2\pi\gamma_{n_1,n_2})\cosh(2\pi\gamma_{n_1,n_2}t_3)\right]}{\gamma_{n_1,n_2}\left[\cosh(2\pi\gamma_{n_1,n_2}) - \cos(2\pi\beta_{n_1,n_2})\right]}. \end{aligned} \tag{3.18}$$

It can be easily seen that, for large γ_{n_1,n_2}, the slowest decaying term on the right hand side of Eq.(3.18) goes as $\exp\left[-2\pi\gamma_{n_1,n_2}(1-t_3)\right]$. So, the fastest convergence now occurs for $t_3 = 0$ and slowest for $t_3 = 0.5$. But even this 'slowest' convergence for $t_3 = 0.5$, amounts to an extremely fast exponential convergence of $\exp(-\pi\gamma_{n_1,n_2})$.

Essentially now the whole problem has reduced to a fast evaluation of G_2 in Eq.(3.16). We take up this case now. As $G_2(\mathbf{r})$ fails to converge fast enough for small separations, we break the sum in Eq.(3.18) into two parts

$$\sum_{n_1,n_2}{}' = \sum_{n_1,n_2'} + \sum_{n_1,n_2=0}{}' . \tag{3.19}$$

Note that in our notation $\sum_n'$ and $\sum_{n'}$ represent the same thing. Thus $G_2(\mathbf{r})$ can be written as

$$G_2(\mathbf{r}) = G_2'(\mathbf{r}) + G_{20}(\mathbf{r}), \tag{3.20}$$

where

$$G_2'(\mathbf{r}) = \frac{4\pi^2}{Vb_3^2} \sum_{n_2}{}' \exp\left(i2\pi n_2 x_2\right) \left(\sum_{n_1=-\infty}^{\infty} \frac{\exp\left(2\pi i n_1 x_1\right) \exp(-2\pi \gamma_{n_1,n_2} t_3)}{\gamma_{n_1,n_2}} \right). \tag{3.21}$$

and

$$\begin{aligned} G_{20}(\mathbf{r}) = & \frac{4\pi^2}{Vb_3^2} \sum_{n_1}{}' \left. \frac{\exp\left[i2\pi n_1 \left(-c_{31} t_3 + t_1\right)\right] \exp(-2\pi \gamma_{n_1,n_2} t_3)}{\gamma_{n_1,n_2}} \right|_{n_2=0,\ \xi=0} \\ & - \frac{4\pi^2}{Vb_3^2} 2\pi t_3. \end{aligned} \tag{3.22}$$

To further transform Eq. (3.22), we express γ_{n_1,n_2} as

$$\begin{aligned} \gamma_{n_1,n_2} &= \left[n_1^2\left(c_{11} - c_{13}^2\right) + n_2^2\left(c_{22} - c_{23}^2\right) + 2n_1 n_2 (c_{12} - c_{13}c_{23}) + \xi^2\right]^{1/2} \\ &= \left(\left[n_1 \widetilde{\delta} + n_2 \widetilde{a}\right]^2 + n_2^2 \widetilde{b}^2\right)^{1/2}, \end{aligned} \tag{3.23}$$

where we have put $\xi = 0$ and

$$\begin{aligned} \widetilde{\delta} &= \left(c_{11} - c_{13}^2\right)^{1/2}, \quad \widetilde{a} = \frac{(c_{12} - c_{13}c_{23})}{\widetilde{\delta}}, \\ \widetilde{b} &= \frac{\left[\left(c_{11} - c_{13}^2\right)\left(c_{22} - c_{23}^2\right) - \left(c_{12} - c_{13}c_{23}\right)^2\right]^{1/2}}{\widetilde{\delta}}. \end{aligned} \tag{3.24}$$

As the convergence of Eq.(3.14) crucially depends on the value of γ_{n_1,n_2}, it is helpful at this point to note that the minimum value of γ_{n_1,n_2} , when both n_1 and n_2 are integers such that they cannot both be zero simultaneously, is given by

$$\gamma_{\min}^2 = \widetilde{b}^2 \min\left(1, \frac{\widetilde{\delta}^2}{\widetilde{a}^2 + \widetilde{b}^2}\right). \tag{3.25}$$

We note that $\gamma_{\min}$ depends upon the geometry of the unit cell. To get a fast convergence, it is imperative that the sides of the triclinic unit cell are labelled such that $\gamma_{\min}$ is as large as possible.

Now, we consider the sum G_{20} defined in Eq.(3.22). Using the relation,

$$V b_3^2 \left|\widetilde{\delta}\right| = 4\pi^2 l_2, \tag{3.26}$$

which is derived in Appendix B, we can write

$$\begin{aligned} G_{20}(\mathbf{r}) &= \frac{\left|\widetilde{\delta}\right|}{l_2} \sum_{n_1}{}' \frac{\exp\left[-2\pi n_1 t_3 \left|\widetilde{\delta}\right|\right]}{|n_1| \left|\widetilde{\delta}\right|} \exp\left(2\pi i n_1 x_1\right) - \frac{2\pi\ t_3 \left|\widetilde{\delta}\right|}{l_2} \\ &= -\frac{1}{l_2} \ln\left[\cosh\left(2\pi t_3 \widetilde{\delta}\right) - \cos\left(2\pi x_1\right)\right] - \frac{\ln(2)}{l_2}, \end{aligned} \tag{3.27}$$

where

$$x_1 = -c_{31} t_3 + t_1,\ x_2 = -c_{32} t_3 + t_2, \tag{3.28}$$

and we have used the identity from Eq.(2.13). Thus, we have been able to obtain $G_{20}(\mathbf{r})$ analytically. Now, we transform $G_2'(\mathbf{r})$. The sum over n_1 in Eq.(3.21) ,

$$S\left(n_2, r_1, r_3\right) = \sum_{n_1=-\infty}^{\infty} \frac{\exp\left(2\pi i n_1 x_1\right) \exp(-2\pi \gamma_{n_1,n_2} t_3)}{\gamma_{n_1,n_2}}, \tag{3.29}$$

can be transformed using an identity,

$$\begin{aligned} &\sum_n \frac{\exp\left(-\beta\sqrt{\alpha^2 + (q+n\delta)^2}\right)}{\sqrt{\alpha^2 + (q+n\delta)^2}} \exp\left[ip\left(q+n\delta\right)\right] \\ &= \frac{2}{|\delta|} \sum_n K_0\left(\alpha\sqrt{\beta^2 + \left(2\pi\frac{n}{\delta} - p\right)^2}\right) \exp\left(2\pi i \frac{n}{\delta} q\right), \end{aligned} \tag{3.30}$$

which can be derived with a simple application of Jacobi Poisson theorem[20] to the integral

$$K_0\left(a\sqrt{b^2 + x^2}\right) = \frac{1}{2} \int_{-\infty}^{+\infty} dy \frac{\exp\left(-b\sqrt{a^2+y^2}\right)}{\sqrt{a^2+y^2}} \exp\left(ixy\right). \tag{3.31}$$

Identifying

$$\beta = 2\pi t_3,\ p = 2\pi\frac{x_1}{\widetilde{\delta}},\ q = n_2 \widetilde{a},\ \alpha = \left|n_2 \widetilde{b}\right| \text{ and } \delta = \widetilde{\delta}, \tag{3.32}$$

one obtains

$$S\left(n_2, r_1, r_3\right) = \exp\left(-2\pi i \frac{x_1}{\widetilde{\delta}} n_2 \widetilde{a}\right) \sum_{n_1=-\infty}^{\infty} \frac{\exp\left(-2\pi t_3 \sqrt{\left|n_2 \widetilde{b}\right|^2 + \left(n_2 \widetilde{a} + n_1 \widetilde{\delta}\right)^2}\right)}{\sqrt{\left|n_2 \widetilde{b}\right|^2 + \left(n_2 \widetilde{a} + n_1 \widetilde{\delta}\right)^2}} \tag{3.33}$$

$$\times \exp\left[2\pi i \frac{x_1}{\widetilde{\delta}} \left(n_2 \widetilde{a} + n_1 \widetilde{\delta}\right)\right]$$

$$= \frac{2}{\left|\widetilde{\delta}\right|} \exp\left(-2\pi i \frac{x_1}{\widetilde{\delta}} n_2 \widetilde{a}\right) \times \sum_{n_1} K_0 \left(2\pi \left|n_2 \widetilde{b}\right| \sqrt{t_3^2 + \left(\frac{n_1 - x_1}{\widetilde{\delta}}\right)^2}\right)$$

$$\times \exp\left(2\pi i \frac{n_1}{\widetilde{\delta}} n_2 \widetilde{a}\right).$$

Substituting the value of $S\left(n_2, r_1, r_3\right)$ in Eq.(3.21) we obtain

$$G_2'(\mathbf{r}) = \frac{2}{l_2} \sum_{n_2}{}' \exp\left[2\pi i n_2 \left(x_2 - \frac{x_1 \widetilde{a}}{\widetilde{\delta}}\right)\right] \tag{3.34}$$

$$\times \sum_{n_1} K_0 \left(2\pi \left|n_2 \widetilde{b}\right| \sqrt{t_3^2 + \left(\frac{n_1 - x_1}{\widetilde{\delta}}\right)^2}\right) \exp\left(2\pi i \frac{n_1}{\widetilde{\delta}} n_2 \widetilde{a}\right).$$

Combining Eqs.(3.20), (3.22) and (3.34) we get one of the main results of this paper,

$$G_2(\mathbf{r}) = \frac{2}{l_2} \sum_{n_2}{}' \exp\left[2\pi i n_2 \left(x_2 - \frac{x_1 \widetilde{a}}{\widetilde{\delta}}\right)\right] \tag{3.35}$$

$$\times \sum_{n_1} K_0 \left(2\pi \left|n_2 \widetilde{b}\right| \sqrt{t_3^2 + \left(\frac{n_1 - x_1}{\widetilde{\delta}}\right)^2}\right) \exp\left(2\pi i \frac{n_1}{\widetilde{\delta}} n_2 \widetilde{a}\right)$$

$$- \frac{1}{l_2} \ln\left[\cosh\left(2\pi t_3 \widetilde{\delta}\right) - \cos\left(2\pi x_1\right)\right] - \frac{\ln\left(2\right)}{l_2}.$$

Result in Eq.(3.35) represents the sum for slab geometry and generalizes the results of Arnold *et al*[14]. Similar expressions were obtained by Liem *et al.*[21]. Substitution of G_2 from Eq.(3.35) in Eq.(3.14) gives us an alternative form of G. We note that the problem of convergence with Eq.(3.35) still persists if the charges are close together. The slowest converging term in Eq.(3.35) goes as $K_0\left(2\pi\left|n_2\right|\rho\right)$ and it still does not converge fast enough when,

$$\rho = \widetilde{b} \sqrt{t_3^2 + \left(\frac{x_1}{\widetilde{\delta}}\right)^2}, \tag{3.36}$$

is small. The problem of convergence lies with only those terms corresponding to $n_1 = 0$. So, we separate out these terms

$$G_2' = G_2'' + G_{1d}, \tag{3.37}$$

where

$$\begin{aligned} G_2'' = {} & \frac{2}{l_2} {\sum_{n_2}}' \exp\left[2\pi i n_2 \left(x_2 - \frac{x_1 \widetilde{a}}{\widetilde{\delta}}\right)\right] \\ & \times {\sum_{n_1}}' K_0 \left(2\pi \left|n_2 \widetilde{b}\right| \sqrt{t_3^2 + \left(\frac{n_1 - x_1}{\widetilde{\delta}}\right)^2}\right) \exp\left(2\pi i \frac{n_1}{\widetilde{\delta}} n_2 \widetilde{a}\right) \end{aligned} \tag{3.38}$$

and

$$\begin{aligned} G_{1d} &= \frac{2}{l_2} {\sum_{n_2}}' \exp\left[2\pi i n_2 \left(x_2 - \frac{x_1 \widetilde{a}}{\widetilde{\delta}}\right)\right] \; K_0 \left(2\pi \left|n_2 \widetilde{b}\right| \sqrt{t_3^2 + \left(\frac{x_1}{\widetilde{\delta}}\right)^2}\right) \\ &= \frac{4}{l_2} \sum_{n_2=1}^{\infty} \cos\left[2\pi n_2 \left(x_2 - \frac{x_1 \widetilde{a}}{\widetilde{\delta}}\right)\right] \; K_0 \left(2\pi n_2 \widetilde{b} \sqrt{t_3^2 + \left(\frac{x_1}{\widetilde{\delta}}\right)^2}\right). \end{aligned} \tag{3.39}$$

The term G_2'' does not have any convergence problem for small separation between the two charges. We need to apply a final transformation to the sum in Eq.(3.39). We start with the identity[2],

$$\begin{aligned} f(\rho, x) &= 4 \sum_{m=1}^{\infty} K_0 (2\pi m \rho) \cos(2\pi m x) \\ &= 2\left\{\gamma + \ln\left(\frac{\rho}{2}\right)\right\} + \frac{1}{\sqrt{\rho^2 + x^2}} \\ &+ \sum_{n_1=1}^{N-1} \left(\frac{1}{\sqrt{\rho^2 + (n_1 + x)^2}} + \frac{1}{\sqrt{\rho^2 + (n_1 - x)^2}}\right) \\ &- 2\gamma - \{\psi(N + x) + \psi(N - x)\} \\ &+ \sum_{l=1}^{\infty} \binom{-1/2}{l} \rho^{2l} \left(\zeta(2l + 1, N + x) + \zeta(2l + 1, N - x)\right), \end{aligned} \tag{3.40}$$

where ψ and ζ stand for digamma and Hurwitz Zeta function respectively. $N \geq 1$ is the smallest integer chosen such that it satisfies the condition $N > \rho + x$. However for better

convergence it is desirable that one chooses N such that $N > \rho + 1$. Now, identifying ρ from Eq.(3.36) and

$$x = \left| \left(x_2 - \frac{x_1 \widetilde{a}}{\widetilde{\delta}} \right) \right| \tag{3.41}$$

and realizing that (see Appendix B)

$$\rho^2 + x^2 = \frac{r_1^2 + r_2^2 + r_3^2 + 2r_1r_2\cos\alpha + 2r_2r_3\cos\beta + 2r_3r_1\cos\gamma}{l_2^2}, \tag{3.42}$$

one obtains an expression for G, which converges exponentially fast even for small x_i:

$$\begin{aligned} G(\mathbf{r}) = {} & \frac{\left|\widetilde{\delta}\right|}{l_2} \sum_{n_1,n_2}{}' \exp\left[2\pi i(n_1t_1 + n_2t_2)\right] \; B(n_1, n_2, r_3, \xi)\Big|_{\xi=0} \\ & + \frac{2}{l_2}\left\{ \sum_{n_1',n_2'} \exp\left[2\pi i n_2 \left(x_2 - \frac{x_1\widetilde{a}}{\widetilde{\delta}}\right)\right] \right. \\ & \times K_0\left(2\pi\left|n_2\,\widetilde{b}\right|\sqrt{t_3^2 + \left(\frac{n_1 - x_1}{\widetilde{\delta}}\right)^2}\right) \left. \exp\left(2\pi i \frac{n_1}{\widetilde{\delta}} n_2 \widetilde{a}\right) \right\} \\ & - \frac{1}{l_2}\ln\left[\cosh\left(2\pi t_3\widetilde{\delta}\right) - \cos\left(2\pi x_1\right)\right] - \frac{\ln(2)}{l_2} + \frac{2\gamma}{l_2} \\ & + \frac{\left|\widetilde{\delta}\right|}{l_2}\frac{\pi}{3}\left(1 + 6t_3^2\right) + \frac{2}{l_2}\ln\left(\frac{\rho}{2}\right) - \frac{\psi(N+x) + \psi(N-x)}{l_2} \\ & + \frac{1}{l_2}\sum_{n=1}^{\infty}\binom{-1/2}{n}\rho^{2n}\left[\zeta\left(2n+1, N+x\right) + \zeta\left(2n+1, N-x\right)\right] \\ & + \frac{1}{l_2}\sum_{n_1=1}^{N-1}\left(\frac{1}{\sqrt{\rho^2 + (n_1+x)^2}} + \frac{1}{\sqrt{\rho^2 + (n_1-x)^2}}\right) \\ & + \frac{1}{\left(r_1^2 + r_2^2 + r_3^2 + 2r_1r_2\cos\alpha + 2r_2r_3\cos\beta + 2r_3r_1\cos\gamma\right)^{1/2}}. \end{aligned} \tag{3.43}$$

Even though Eq.(3.43) gives a very good convergence for smaller values of $r_i < \varepsilon = 10^{-3}$, it is not defined when $t_3 = 0$ and $x_1 = 0$. The problem lies in the logarithmic terms, which can be combined together such that the opposing logarithmic divergences cancel each other as shown below. For small separations, it can be easily shown[7] that

$$\begin{aligned} \ln\left[\cosh y - \cos x\right] = {} & \ln\left[\frac{y^2 + x^2}{2}\right] + \ln\left\{1 + \frac{2!}{4!}\left(y^2 - x^2\right) + \frac{2!}{6!}\left(y^4 - x^2y^2 + x^4\right)\right. \\ & \left. + \frac{2!}{8!}\left(y^4 + x^4\right)\left(y^2 - x^2\right) + \mathrm{O}\left[x^8, y^8\right]\right\}. \end{aligned} \tag{3.44}$$

Thus all of the logarithmic terms in Eq.(3.43) can be combined together as

$$
\begin{aligned}
&-\frac{1}{l_2}\ln\left[\cosh\left(2\pi t_3\widetilde{\delta}\right)-\cos\left(2\pi x_1\right)\right]-\frac{\ln(2)}{l_2}+\frac{2}{l_2}\ln\left(\frac{\rho}{2}\right) \\
&=-\frac{2}{l_2}\ln\left(\frac{4\pi\widetilde{\delta}}{\widetilde{b}}\right)+\ln\left\{1+\frac{2!}{4!}\left[\left(t_3\widetilde{\delta}\right)^2-x_1^2\right]+\frac{2!}{6!}\left[\left(t_3\widetilde{\delta}\right)^4-x_1^2\left(t_3\widetilde{\delta}\right)^2+x_1^4\right]\right. \\
&\left.+\,+\frac{2!}{8!}\left[\left(t_3\widetilde{\delta}\right)^4+x_1^4\right]\left[\left(t_3\widetilde{\delta}\right)^2-x_1^2\right]+\mathrm{O}\left[x_1^8,\left(t_3\widetilde{\delta}\right)^8\right]\right\}.
\end{aligned}
\tag{3.45}
$$

The RHS of Eq.(3.45) remains regular even when x_1 and t_3 both tend to zero. The self-energy of the system can be easily obtained now as,

$$
G_{\mathrm{self}}^{3\mathrm{D}}(\mathbf{r})=\lim_{(r_1,r_2,r_3)\to(0,0,0)}\left(G(r_1,r_2,r_3)-\frac{1}{\left(r_1^2+r_2^2+r_3^2+2r_1r_2\cos\alpha+2r_2r_3\cos\beta+2r_3r_1\cos\gamma\right)^{1/2}}\right)
\tag{3.46}
$$

$$
\begin{aligned}
&=\frac{\left|\widetilde{\delta}\right|}{l_2}\sum_{n_1,n_2}{}^{\prime}\left.B(n_1,n_2,0,\xi)\right|_{\xi=0}+\frac{2}{l_2}\sum_{n_1',n_2'}K_0\left(2\pi\left|n_1n_2\frac{\widetilde{b}}{\widetilde{\widetilde{\delta}}}\right|\right)\times\exp\left(2\pi i n_1n_2\frac{\widetilde{a}}{\widetilde{\widetilde{\delta}}}\right) \\
&+\frac{\left|\widetilde{\delta}\right|}{l_2}\frac{\pi}{3}-\frac{2}{l_2}\ln\left(\frac{4\pi\widetilde{\delta}}{\widetilde{b}}\right)+\frac{2\gamma}{l_2}.
\end{aligned}
$$

We have thus obtained complete expressions for G and the self-energy.

IV. RESULTS AND CONCLUSIONS

We have obtained complete expressions for the logarithmic potential in 2D and Coulomb potential in 3D, including the self-energies. The results were derived for most general cases, that is a rhombic cell in 2D and a triclinic cell in 3D. To my knowledge, this is the first time a practical method has been developed in 3D, which is different from the Ewald method, and yet may be applied to a triclinic unit cell to obtain periodic Coulomb sums. Even though the formulas developed here look complicated, their implementation on a computer will be marginally difficult from the case of orthorhombic unit cell. The formulas derived here converge extremely fast and require only a few dozen terms at worst to obtain results to a very high accuracy as opposed to the Ewald method, which may require close to 200 to 300 terms for the same calculations. In the process, we have simplified and solved a problem mentioned by Crandall[10], that of finding Coulomb potential in close vicinity of a particle

under the PBC. An important implication of the formulas derived here is that most part of the interaction can be calculated linearly in the number of charges present in the system. For more details on how this can be achieved, we refer the reader to Sperb who discusses this in the context of an orthorhombic cell. The results obtained in this paper reduce to the results of a recent paper[7] when all angles pertaining to the unit cell are set to $\pi/2$.

The results for 3D triclinic case may be obtained by directly generalizing Lekner's work. This work by the author will be presented elsewhere. We also note that the logarithmic sum in 2D for a rhombic cell may be obtained in a closed form. This will be the subject of another paper. Also, here we would like to point out a connection between the results of slab geometry and that of 3D triclinic cell. As it has been shown here, the 3D Green function can be broken in two parts. The first part corresponds to the slab geometry Green function and the second part takes into account the rest of the layers. Thus following Ref.16 one can make use of this relation to obtain potential energies for the slab geometry cases by employing the result for the triclinic cell.

A naive application of most methods gives a scaling which goes as N^2, where N is the number of charges in the unit cell. However, the Ewald method can be optimized[12] to give a scaling of $[N \ln(N)]^{3/2}$. Strebel *et al.*[11] gave an approximate method, which they call the MMM method, which is based on the formulas developed by Sperb in his earlier work[2]. With the help of MMM one can achieve a $N \ln(N)$ scaling. There is another approximate method in use to achieve a faster scaling. This method is known as PPPM. In Ref.11, however, it was shown that for $N > 2^{10}$ and a relative tolerance of 10^{-4} the MMM is the best method available. As the formulas derived here are a generalization of Sperb's work, it may now be possible, by using the results presented in this work, to employ the MMM method to achieve a scaling of $N \ln(N)$ even for a triclinic cell. Similarly for the logarithmic interaction in 2D, it should be possible to achieve $N \ln(N)$ scaling.

In short, we believe the method developed here is an alternative to the Ewald method. The formulas developed here generalize and simplify Sperb's[2] work. From the results of summation formula derived for a triclinic cell, it is easy to obtain results for $2D + h$ slab geometry and vice versa. For the slab geometry case expressions obtained here generalize the work of Arnold *et al*[14]. and give an alternate derivation of the results obtained by Liem *et al.*[21]. The formulas derived in this work can be easily employed to calculate the Madelung potential for any periodic crystal in 3D, where a triclinic cell repeats itself to infinity under

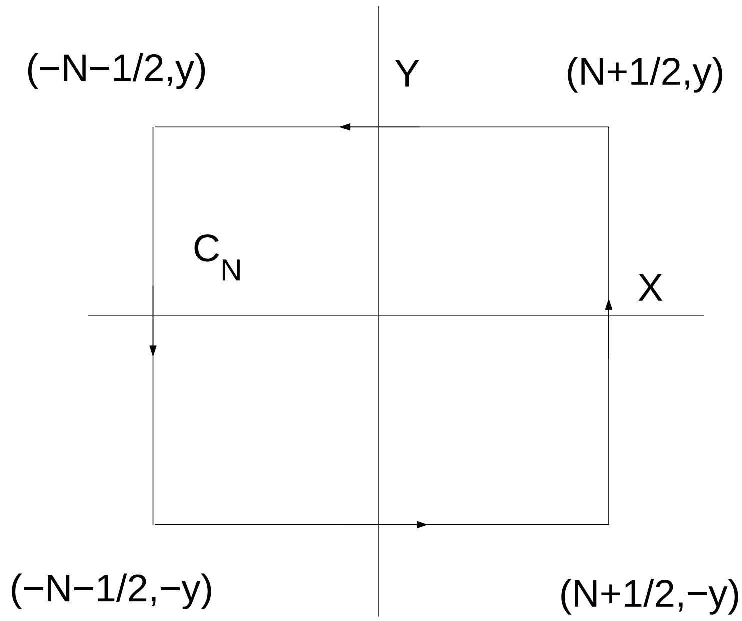

FIG. 2: Contour of integration, C_N. Both N and y tend to infinity.

the PBC.

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APPENDIX A: COMPLEX SUM

The usual way to sum over series of type

$$S = \sum_{n=-\infty}^{\infty} f(n) \tag{A1}$$

is to consider the integral

$$I = \oint f(z)\, \pi \cot(\pi z)\, dz. \tag{A2}$$

It is required that the function $f(z)$ satisfies the condition that integral I becomes zero when the contour of integration is chosen to be C_N as shown in Fig.2.

The poles of $\pi \cot(\pi z)$ fall at $z = n$ where $n = 0, \pm 1, \pm 2, \ldots$. Then by residue theorem we have

$$\sum_{n=-\infty}^{\infty} f(n) = -\text{sum of residues of } f(z)\, \pi \cot(\pi z) \text{ at the poles of } f(z)\,. \tag{A3}$$

Here, in particular, we consider the function

$$f(n) = \frac{\exp(in\alpha)}{(n-\beta)^2 + \gamma^2} \qquad \alpha < 2\pi, \tag{A4}$$

where x, β, γ are real numbers and $x > 0$. The results obtained here are more general in nature and may be applied for other forms of $f(n)$. It can be easily verified that the function given above does not satisfy the condition that integral I go to zero for contour C_N. A trick which is usually not found in books may help solve the problem. Instead of considering the integral I in Eq.(A2), we consider the following integral

$$I' = \oint f(z)\, (-1)^z\, \pi \csc(\pi z)\, dz, \tag{A5}$$

where have in mind that $\exp(-i\pi) = -1$. Residues of $f(z)(-1)^z \pi \csc(\pi z)$ at $z = n$, $n = 0, \pm 1, \pm 2, \ldots$, is

$$\lim_{z \to n} f(z)\,(z-n)\,(-1)^z \pi \csc(\pi z) = f(n)\,. \tag{A6}$$

Thus if the integral I' goes to zero for the contour C_N then we obtain

$$\sum_{n=-\infty}^{\infty} f(n) = -\text{sum of residues of } f(z)\,(-1)^z \pi \csc(\pi z) \text{ at the poles of } f(z)\,. \tag{A7}$$

Function f given in Eq.(A4) does satisfy the condition that $I' = 0$ when the integration is evaluated for the contour C_N. To show this, we concentrate on the the following function

$$g(x, y, \alpha) = \frac{\exp(iz\alpha)\exp(-i\pi z)}{\sin(\pi z)}. \tag{A8}$$

We note that in terms of $g(x, y, \alpha)$, $f(z)$ can be written as

$$f(z) = \frac{g(x, y, \alpha)}{(n-\beta)^2 + \gamma^2}. \tag{A9}$$

With the substitution of $z = x + iy$ in Eq. (A8), we obtain

$$|g(x, y, \alpha)| = \frac{2\exp(-y\alpha)}{\left[\exp(-4\pi y) - 2\cos(2\pi x)\exp(-2\pi y) + 1\right]^{1/2}}. \tag{A10}$$

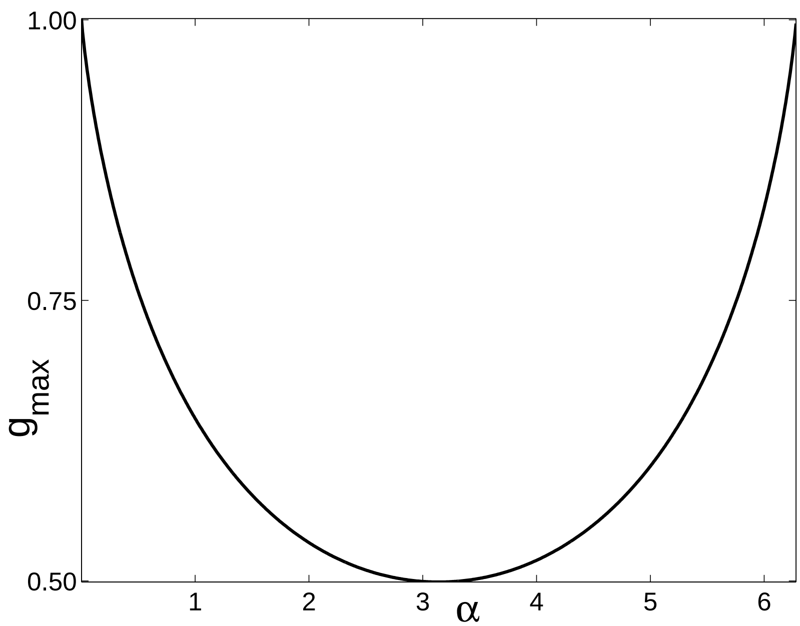

FIG. 3: The value of function $g_{\max}$ remains between 0.5 and 1.0 as α is varied from 0 to 2π.

We note that

$$\lim_{|y|\to\infty} |g(x, y, \alpha)| = 0. \tag{A11}$$

The condition in Eq. (A11) ensures that I' goes to zero on those portions of the contour which lie parallel to the x axis. To consider the portions of contour parallel to the y axis, we substitute $x = N + 1/2$. One obtains

$$|g(N + 1/2, y, \alpha)| = \frac{2\exp(-y\alpha)}{1 + \exp(-2\pi y)}, \tag{A12}$$

which implies that the maximum value of the function $|g(N + 1/2, y, \alpha)|$ occurs for

$$y = \frac{1}{2\pi} \ln\left(\frac{2\pi - \alpha}{\alpha}\right), \tag{A13}$$

and is given by

$$g_{\max}(\alpha) = \frac{2\pi - \alpha}{2\pi} \exp\left[-\frac{\alpha}{2\pi} \ln\left(\frac{2\pi - \alpha}{\alpha}\right)\right]. \tag{A14}$$

A plot of $g_{\max}(\alpha)$ is shown in Fig.3.

It is clear that the value of $g_{\max}(\alpha)$ remains between 0.5 and 1.0, and this ensures $|f(z)z|$ goes to zero on the contours parallel to the y axis. Thus it is clear that I' goes to zero when

evaluated for the contour C_N and hence by the application of formula in Eq. (A7) we obtain

$$\begin{aligned}\sum_{n=-\infty}^{\infty}\frac{\exp\left(in\alpha\right)}{\left(n-\beta\right)^2+\gamma^2} &= -\frac{\exp\left[\left(\beta+i\gamma\right)\left(\alpha+i\pi\right)\right]}{2i\gamma}\pi\csc\left[\pi(\beta+i\gamma)\right] \\ &- \frac{\exp\left[\left(\beta-i\gamma\right)\left(\alpha+i\pi\right)\right]}{-2i\gamma}\pi\csc\left[\pi(\beta-i\gamma)\right] \\ &= \frac{\pi}{\gamma}\frac{\exp\left[i\beta\left(\alpha-2\pi\right)\right]\sinh\left(\gamma\alpha\right)+\exp\left(i\beta\alpha\right)\sinh\left[\gamma\left(2\pi-\alpha\right)\right]}{\cosh\left(2\pi\gamma\right)-\cos\left(2\pi\beta\right)}.\end{aligned} \tag{A15}$$

APPENDIX B: TRICLINIC CELL

Let us consider the most general type of triclinic cell shown in the Fig.4. The cell is characterized by sides l_1, l_2 and l_3 and angles α, β and γ. We can choose the unit vectors along the directions of the triclinic cell as

$$\begin{aligned} e_1 &= (1,0,0)\,, \\ e_2 &= (\cos\alpha,\sin\alpha,0) \\ e_3 &= \left(\cos\gamma,\frac{\cos\beta-\cos\alpha\cos\gamma}{\sin\alpha},\left[\sin^2\gamma-\left(\frac{\cos\beta-\cos\alpha\cos\gamma}{\sin\alpha}\right)^2\right]^{1/2}\right).\end{aligned} \tag{B1}$$

We can now get reciprocal vectors using equation. Now we can calculate c_{ij} and we get the following results using the package Mathematica

$$\begin{aligned} c_{11} &= \frac{l_3^2}{l_1^2}\frac{\sin^2\beta}{\sin^2\alpha},\ c_{22}=\frac{l_3^2}{l_2^2}\frac{\sin^2\gamma}{\sin^2\alpha},\ c_{33}=1, \\ c_{12} &= \frac{l_3^2}{l_1l_2}\left(\frac{-\cos\alpha+\cos\beta\cos\gamma}{\sin^2\alpha}\right), \\ c_{23} &= \frac{l_3}{l_2}\left(\frac{-\cos\beta+\cos\alpha\cos\gamma}{\sin^2\alpha}\right), \\ c_{13} &= \frac{l_3}{l_1}\left(\frac{-\cos\gamma+\cos\alpha\cos\beta}{\sin^2\alpha}\right).\end{aligned} \tag{B2}$$

We can then obtain ρ and x as follows

$$\rho=\frac{\left(r_1^2\cos^2\alpha+r_3^2\cos^2\beta+2r_1r_3\times\left[\cos\gamma-\cos\alpha\cos\beta\right]\right)^{1/2}}{l_2} \tag{B3}$$

and

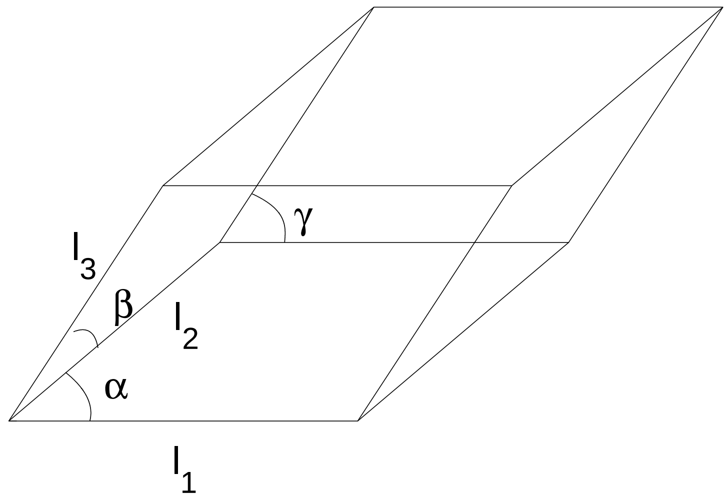

FIG. 4: A triclinic cell explaing different labels for sides and angles.

$$x = \frac{r_2 + r_1 \cos\alpha + r_3 \cos\beta}{l_2}. \tag{B4}$$

Finally we obtain

$$\rho^2 + x^2 = \frac{r_1^2 + r_2^2 + r_3^2 + 2r_1 r_2 \cos\alpha + 2r_2 r_3 \cos\beta + 2r_3 r_1 \cos\gamma}{l_2^2}. \tag{B5}$$

Using the relations given above, it can be shown on Mathematica that

$$V b_3^2 \left|\widetilde{\delta}\right| = 4\pi^2 l_2, \tag{B6}$$

where b_3, V and $\widetilde{\delta}$ are defined in Eqs. (3.5), (3.2) and (3.24).

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